

Extraction of cellulose with subcritical and supercritical ethanol¹

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Abstract Cotton cellulose was extracted with ethanol in sub- and supercritical states dynamically. The degree of conversion was 95.4% and the extract yield was 55.2% when cotton cellulose was non-isothermally extracted with ethanol from 20°C to 400°C. From an engineering standpoint, in the temperature range from 200°C to 320°C, the rate of extract formation could adequately be described by a second-order reaction kinetics equation with the activation energy of 105.3 kJ/mol and the pre-exponential factor of $3.53 \times 10^7 \text{ s}^{-1}$. With the non-isothermal experimental technique, it was possible to determine the kinetic parameters; conversion degree and extract yield by one experiment.

Key words: Cellulose, Ethanol, Supercritical fluid extraction, Thermal decomposition

Introduction

As a result of the public's increasing environmental awareness, the researches focused on developing processes that utilize low toxic organic solvents have flourished in the past 10 years. Most of these researches have examined the possibility of using supercritical and slightly subcritical fluids as extraction and reaction solvents (Reaves 1999).

Supercritical fluid extraction of lignocellulosic materials from biomass is similar to pyrolysis, which is used to convert biomass to useful chemicals or fluid fuels (Goto 1990). The pyrolysis of biomass can yield char as well as a variety of volatile products. The char formation reduces the yield of volatiles and causes poor heat transfer. These problems can be ameliorated by employing supercritical fluid extraction, that is, thermal decomposition with supercritical fluid (Koll 1978; Labrecque 1984; Poirier 1987). When the pyrolysis of biomass is carried out with supercritical fluid, the intermediate reaction products that form char are readily extracted due to the high solubility in supercritical fluid.

Because cellulose comprises about 50% of most biomass materials, its pyrolytic behaviors in supercritical fluid have attracted special attention. Koll and Metzger (1978) compared the supercritical acetone extraction of cellulose and its pyrolysis. By using supercritical fluid, char formation was reduced to 2%, while pyrolysis produced 34% (under nitrogen) or 18% (under vacuum) char. The main products of the

supercritical acetone extraction were anhydrosugars, and a higher yield of glucosan was obtained than for the pyrolysis under vacuum (Koll 1978). Goto *et al.* (1990) investigated the thermal decomposition and extraction with supercritical tert-butyl alcohol of cellulose from wood pulp dynamically. The extraction rate increased markedly with temperature. A first-order three-reaction model was applied to the reaction-extraction process. The predicted extraction rate for this model agreed well with the experimental data (Goto 1990).

The aim of this study was to obtain detailed information on the thermal decomposition of cellulose during sub- and supercritical ethanol extraction by using the non-isothermal experimental technique, and to calculate the activation energy and the pre-exponential factor with a reaction-kinetics model.

Experimental methods

The experiment was carried out dynamically in a flow-through apparatus (Fig.1). The reactor consisted of a thick-walled pressure jacket with a removable internal material vessel, in which the material bed was fixed between two stainless steel filter plates. The reactor system as well as the entering pressurized ethanol were slowly heated ($2.5 \text{ K} \cdot \text{min}^{-1}$) from 20°C to 400°C. The pressure in the reactor was fixed at 13 MPa ($P_r=2.01$).

The ethanol flowed around the internal material vessel before entering the material bed through the lower filter plate. It became to charge with extract and with liquid and gaseous decomposition products while passing through the material bed. The extract content of the ethanol and the volume of the gaseous decomposition products were measured in short time intervals with increasing temperature and were used

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to calculate the rates of formation and integral yields of the extract and gas. The flow rate of the solvent ($7.5 \text{ mL} \cdot \text{min}^{-1}$) was held constant during the experiment.

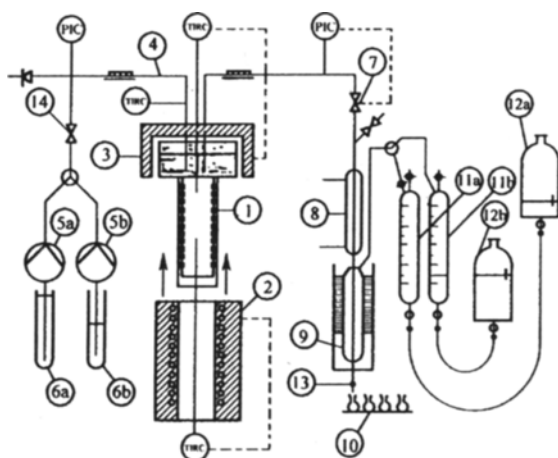


Fig.1. Non-isothermal extraction system

1. Reactor; 2. Oven; 3. Flange heater; 4. Solvent preheater;
5. Pumps; 6. Solvent reservoirs; 7. Needle valve; 8. Cooler;
9. Ice-bath; 10. Flasks; 11. Gas sampling; 12. Level bottles;
13. Extract outlet; 14. Non-return valve

Results and discussion

Extraction rate and yield

The degree of conversion was 95.4% when cotton cellulose was non-isothermally extracted with ethanol from 20°C to 400°C . This value was slightly lower than that of the extraction of cellulose with supercritical acetone at $250 - 340^\circ\text{C}$ (98%) achieved by Koll and Metzger (1978). After the extraction, the remaining residue in the reactor was black solid (4.6%), presumed to be char as in the case of pyrolysis. Thus, a part of the cellulose decomposed to the derivatives and was extracted into the supercritical solvent, while the remainder of the cellulose became char. This result indicated that supercritical ethanol could improve heat transfer and restrain char formation. From Fig.2 it can be seen that the extraction of cotton cellulose with ethanol began at about 200°C and ended at about 370°C . The extract yield increased when the temperature increased from 200°C to 370°C , and the maximum formation rate appeared at about 250°C , which was close to the critical temperature of ethanol (243°C).

The gas formation rate and yield gradually increased as the temperature increased from 150°C to 320°C , and markedly increased after the temperature reached at 320°C (Fig.3). This result showed that the gasification of cellulose mainly occurred at the temperature range between 320°C and 400°C .

The water-insoluble matters mainly generated at the temperature between 210°C and 310°C (Fig.4).

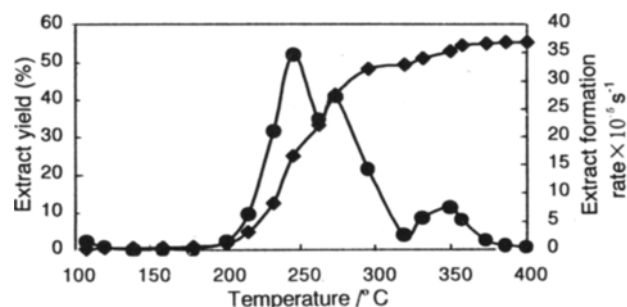


Fig. 2. Variation of extract yield (♦) and extract formation rate (•) with temperature

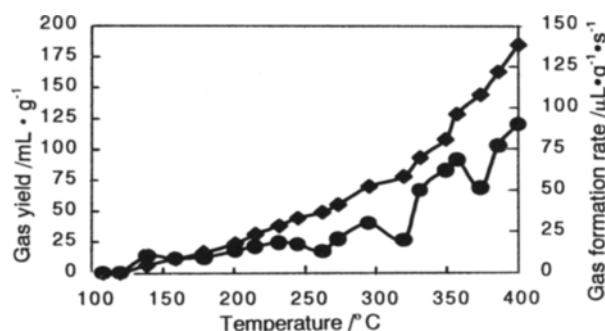


Fig. 3. Variation of gas yield (♦) and gas formation rate (•) with temperature

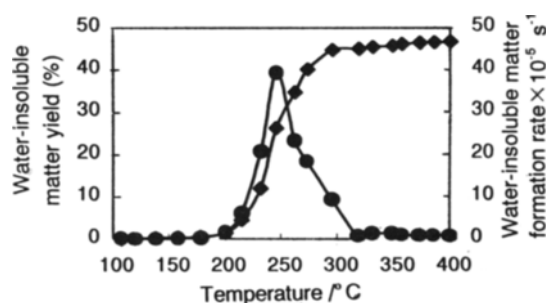


Fig. 4. Variation of water-insoluble matter yield (♦) and water-insoluble matter formation rate (•) with temperature

Kinetics of extract formation

In this experimental condition, the size of cellulose was very small, the rate of solvent was large, and the diffusivity of sub- and supercritical fluid was high. Thus, the effect of some physical factors such as diffusion on extraction process can be negligible, while the extract formation rate is controlled by chemical reaction rate mainly. It is assumed that the extract is formed in one step by the decomposition and solvolysis of cellulose, the chemical reaction can

be expressed as follows:

cellulose $\xrightarrow[\text{solvent}]{\text{decomposition and solvolysis}}$ cellulose derivatives

At the same time, it is assumed that the extract formation rate only relates to the extractable matter of cellulose. Hence, the following equation can be obtained according to the kinetics definition:

$$dx/dt = k(1-x)^n \quad (1)$$

$$x = \frac{m_{E(t)}}{m_{E(\infty)}} = \frac{m_{E(t)}/m_0}{m_{E(\infty)}/m_0} = \frac{y_{E(t)}}{y_{E(\infty)}} \quad (2)$$

Where

$m_{E(t)}$ -- the extract mass at time t (g);
 $m_{E(\infty)}$ -- the maximum extractable mass (g);
 m_0 -- the mass of cellulose (g);
 $y_{E(t)}$ -- the extract yield at time t (%);
 $y_{E(\infty)}$ -- the maximum extract yield (%);
 k -- the kinetics rate constant, which relates to temperature:

$$k = k_0 \exp(-E_a/RT) \quad (3)$$

Where

k_0 -- the pre-exponential factor (s^{-1});
 E_a -- the activation energy of reaction (J/mol);
 R -- the molar gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$);
 T -- the temperature (K);
 n -- the reaction order;
 t -- the time (s).

Substituting Equation (2) and (3) into Equation (1) gives:

$$\frac{dy_{E(t)}}{dy_{E(\infty)} \cdot dt} = k_0 \exp(-E_a/RT) \left(1 - \frac{y_{E(t)}}{y_{E(\infty)}}\right)^n \quad (4)$$

Because the extract formation rate at time t , $r_{E(t)}$ is equal to $dy_{E(t)}/dy_{E(\infty)}$, substituting $r_{E(t)} = dy_{E(t)}/dy_{E(\infty)}$ into Equation (4) and rearranging gives:

$$\frac{r_{E(t)} \cdot y_{E(\infty)}^{(n-1)}}{[y_{E(\infty)} - y_{E(t)}]^n} = k_0 \exp(-E_a/RT) \quad (5)$$

Taking logarithms of Equation (5) gives:

$$\ln \frac{r_{E(t)} \cdot y_{E(\infty)}^{(n-1)}}{[y_{E(\infty)} - y_{E(t)}]^n} = \ln k_0 - E_a/RT \quad (6)$$

After the reaction order n is selected, one straight line can be obtained by plotting the left-hand side of Equation (6) vs. $1/T$. The slope and intercept are $-E_a/R$ and $\ln k_0$ respectively. Therefore, E_a and k_0 can be obtained.

In this paper, the probe difference method was applied to the determination of the reaction order n according to the linear correlatively. The results are shown in Table 1. From an engineering standpoint, in the temperature range from 200°C to 320°C, the rate of extract formation could adequately be described by a second-order reaction kinetics with the activation energy of 105.3 kJ/mol and the pre-exponential factor of $3.53 \times 10^7 \text{ s}^{-1}$. The kinetics equation is as follows:

$$dx/dt = 3.53 \times 10^7 \exp(-105300/T) (1-x)^2$$

Table 1. Kinetics parameters at various reaction order n at 200-320°C

Reaction order (n)	Activation energy (E_a) / $\text{kJ} \cdot \text{mol}^{-1}$	Pre-exponential factor (k_0) / s^{-1}	Correlation coefficient (r)
0.5	26.4	1.15×10^{-1}	-0.425 55
1	54.4	1.19×10^2	-0.725 56
1.5	79.8	6.48×10^4	-0.852 81
2	105.3	3.53×10^7	-0.914 21

Conclusions

The thermal decomposition and extraction of cotton cellulose with sub- and supercritical ethanol were dynamically investigated by using the non-isothermal experimental technique. The degree of conversion was 95.4%, and the extract yield was 55.21% when cotton cellulose was non-isothermally extracted with ethanol from 20°C to 400°C. From an engineering

standpoint, in the temperature range from 200°C to 320°C, the rate of extract formation could adequately be described by a second-order reaction kinetics equation with the activation energy of 105.3 kJ/mol and the pre-exponential factor of $3.53 \times 10^7 \text{ s}^{-1}$. It was possible to determine the kinetic parameters as well as conversion degree and extract yield in one experiment.

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References

- Goto, M., Hortacsu, O., and McCoy, B.J. 1990. Supercritical thermal decomposition of cellulose: experiments and modeling. *Ind. Eng. Chem. Res.*, **29** (7): 1091
- Koll, P. and Metzger, J. O. 1978. Thermal degradation of cellulose and chitin in supercritical acetone. *Angew. Chem. Int. Ed. Engl.*, **17** (10): 754
- Labrecque, R., Kaliaguine, S. and Grandmaison, J.L., 1984. Supercritical pyrolysis of wood. *Ind. Eng. Chem. Prod. Res. Dev.*, **23** (1): 177
- Poirier, M.G., Ahmed, A., Grandmaison, J.L. *et al.*, 1987. Supercritical gas extraction of wood with methanol in a tubular reactor. *Ind. Eng. Chem. Res.*, **26** (9): 1738
- Reaves, J.T. and Roberts, C.B. 1999. Subcritical solvent effects on a parallel Diels-Alder reaction network. *Ind. Eng. Chem. Res.*, **38** (3): 855